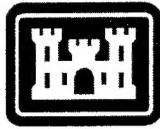


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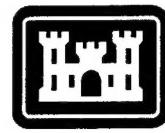
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Evaluation of H.E.L.P. Mate 2000 for the Identification and Quantification of Petroleum Hydrocarbon Products

Alan D. Hewitt

September 2000

Technical Report
ERDC/CRREL TR-00-20



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of Engineers®**
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Alan D. Hewitt

September 2000

Prepared for
RAPID COMMERCIALIZATION INITIATIVE

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Abstract: The H.E.L.P. Mate 2000 (HM 2000) is a spectrophotometric instrument developed for use with the Hanby Test Kits to rapidly assess of total petroleum hydrocarbon contamination (TPH) in environmental matrices on site. This spectrophotometer is designed to remove the subjectivity associated with the present visual method of analysis, and to eliminate the requirement for prior knowledge of the type of petroleum hydrocarbon contamination present at a given site. Both the HM 2000 and the current visual method of analysis

measure the color that is produced by the Friedel-Crafts reaction with the aromatic hydrocarbons present in petroleum-based fuels, oils, and solvents. Laboratory and field studies were used to evaluate the HM 2000. Different results were obtained, depending on the type of sample matrix. In general, the HM 2000 was more accurate and precise for soil samples than for water samples. However, in comparison to the visual method, the HM 2000 was neither as accurate nor did it offer any qualitative advantages.

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PREFACE

This report was prepared by Alan D. Hewitt, Research Physical Scientist, Geological Sciences Division, U.S. Army Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory, Hanover, New Hampshire.

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Evaluation of H.E.L.P. Mate 2000 for the Identification and Quantification of Petroleum Hydrocarbon Products

ALAN D. HEWITT

INTRODUCTION

This study evaluates the H.E.L.P. Mate 2000 (HM 2000), a spectrophotometric device for determining the extent and type of total petroleum hydrocarbon (TPH) contamination in soil and water matrices. This field-portable instrument was designed to be used in conjunction with Hanby Test Kits for soil and water samples. Each matrix-specific test kit contains the necessary reagents and equipment for extracting TPH from an environmental matrix and for performing a Friedel-Crafts reaction that changes the catalyst's color. This method, which is based on a visual inspection of the color and intensity of an insoluble catalyst, has been marketed for the detection and semi-quantification of some aromatic hydrocarbons and TPH.

The U.S. Environmental Protection Agency's underground storage tank program (USEPA 1997) acknowledges the utility of these field kits, and states that they are capable of establishing the presence of contamination (i.e., yes/no) and an order of magnitude estimate of concentration. To improve on the data quality, the manufacturer of these test kits developed a field-portable spectrophotometer and data evaluation system, the HM 2000. A direct reading from the HM 2000 should remove the subjectivity associated with visually interpreting the catalyst's color for quantification, and may, in the future, also allow the type of TPH pollution to be interpreted.

The HM 2000 was used to estimate the concentration of TPH in both fortified and field-contaminated samples. Laboratory studies were conducted at CRREL, and the device was demonstrated in the field at the Naval Construction Battalion Center, Port Hueneme, California, an Advance Fuel Hydrocarbon National Environmental Technology Test Site (U.S. Navy 1999). The laboratory experiments were performed by the author of this report, while the field exercise was conducted

by the developer of the Hanby Test Kits and the HM 2000 analyzer, with help from an assistant (called from here on the technology developer). The same HM 2000 system was used for both trials. This report will address the ease of use, reliability, accuracy, and the precision of the HM 2000.

TECHNOLOGY DESCRIPTION

Color chemistry

Both the visual and the HM 2000 methods of analysis assess the intensity of visible colors that are formed when aromatic compounds have alkylhalide groups attached to them through the Friedel-Crafts alkylation reaction process. This colorimetric method can be used to measure individual aromatic compounds (i.e., benzene, toluene, xylenes, etc.) or mixtures, as exist in petroleum fuels and oils (i.e., gasoline, diesel fuel, and motor oil). For petroleum fuels and oils, the resultant color intensity can be used to estimate the TPH concentration in an environmental sample. The reagents used in the Hanby Test Kits for the Friedel-Crafts alkylation reaction are aluminum trichloride (AlCl_3), a strong Lewis acid as the catalyst, and carbon tetrachloride (CCl_4) as the source of alkyl (alkylhalide) groups that are attached to aromatic hydrocarbons. The electrophilic substitution that occurs once the aluminum trichloride is introduced results in the formation of very large molecules with a high degree of electron dislocation, creating a color on the surface of the catalyst.

Soil sample preparation

For soils, instructions supplied with the Hanby Test Kit recommend placing 5 g into a tared 50-mL beaker and weighing, then adding 10 mL of an extraction solvent composed of 20% carbon tetrachloride/80% n-heptane (v/v). After 2 to 3 minutes of vigorous stir-

ring with a metal spatula to disperse the soil, the solvent/extract is allowed to separate, and 4.2 mL of the clear solvent phase is decanted into a specially designed optical cuvette (a mark on the wall of the vessel denotes the correct volume). Next, 0.5 g of aluminum trichloride is poured into the cuvette, which is then capped. The cuvette is intermittently shaken for periods of 15 seconds, over a 2- to 3-minute period. Lastly, the catalyst is allowed to settle to the bottom of the cuvette, creating a 1- to 2-cm-thick layer.

Water sample preparation

For water samples, the kit instructions recommend transferring 500 mL to a separatory funnel, followed by 5 mL of carbon tetrachloride. The capped separatory funnel is then gently agitated to completely intersperse this immiscible solvent throughout the aqueous phase while periodically venting to release any pressure buildup. This extraction step takes 3 minutes; then the separatory funnel is returned to a ring stand to allow the solvent to separate. While the solvent separates from the water phase, the stem of the separatory funnel should be dried with a rolled up paper towel. Once the solvent settles to the bottom of the funnel, this layer is drained into a cuvette, filling it to the 4.2-mL mark. After the cuvette is checked for water droplets clinging to the walls (if water is present, the solvent should be transferred to a second optical tube), 0.5 g of aluminum trichloride is added and the cuvette capped and shaken as described previously.

Visual analysis

The sample preparation steps for soil and water samples are identical for both the visual and HM 2000 methods, with the exception of the amount of catalyst that is used. The reference photo color charts (standards) supplied with the kits for the visual analysis were made by preparing samples with known concentrations of commercial petroleum products and processing them through the steps appropriate for either a soil or water matrix. When these standard charts were made, 1.0 g of aluminum trichloride was used for the Friedel-Crafts reaction, twice the amount that is currently used. To correct for the decreased volume of catalyst, it is recommended that photo chart concentration be halved, after the sample's color intensity is matched to the chart.* The visual assessment should be made about 4 minutes after adding the catalyst.

HM 2000 analysis

The HM 2000 measures reflectance in the visible region (400–750 nm) of the energy spectrum using a

charged-couple device (CCD) 2048 linear array detector (Ocean Optics, Inc., Dunedin, Florida). A tungsten-halogen bulb gives full-spectrum light energy that is focused on the catalyst after it passes through a fiber optic transmission line, and the energy that is not absorbed by the sample is reflected back to the detector for measurement. Both the light source and detector are directed at the catalyst through the bottom of the cuvette. The cuvettes are manufactured specifically for this spectrophotometer, and have a fused optical bottom that provides a flat surface for the transmission of light. In addition, these vessels were marked on the wall for proper orientation in the spectrophotometric analysis chamber.

The signal obtained by the detector is processed by notebook computer, which gives nearly instantaneous analysis of the intensity over a specified wavelength interval. In general, the amount of reflectance measured by the detector is inversely proportional to the amount of a petroleum product in the environmental matrix being tested. In addition, since the detector is capable of measuring discrete energies of the chromophoric (color-producing) Friedel-Crafts reaction products from different petroleum fuels, oils, and solvents, this technique potentially allows for a qualitative interpretation. Figure 1 shows some energy spectra obtained with the HM 2000 for gasoline- and diesel-fuel-contaminated soil samples. Samples were measured with the HM

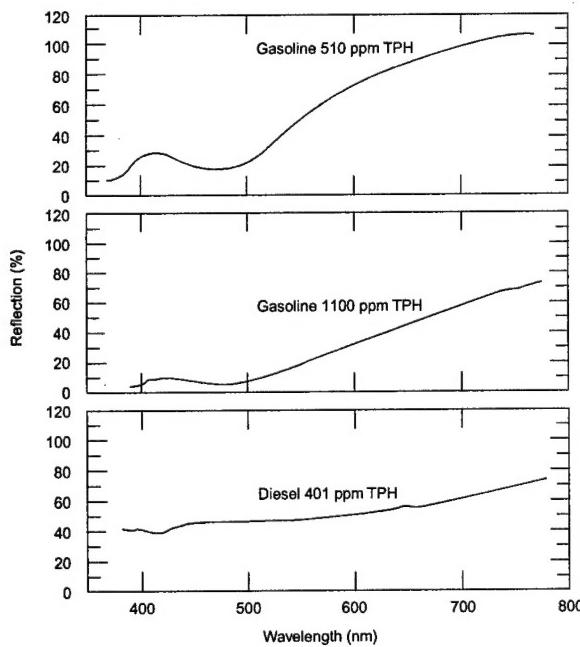


Figure 1. Energy spectra obtained with the HM 2000 for gasoline- and diesel-fuel-contaminated soil samples.

* Personal communication with John Hanby, H.E.L.P., Inc, 1999.

2000, 10 minutes after the catalyst was added. Samples can be prepared and analyzed by both methods within 15 minutes. Like the visual method of analysis, the HM 2000 requires the development of calibration models for each type of petroleum contamination and sample matrix. Therefore, it is necessary to prepare standards of the different commercial petroleum products and process them through the steps appropriate for either a soil or water matrix.

Detection range

The detection limits for TPH associated with both gasoline and diesel fuel contamination in environmental matrices for the HM 2000 have been reported to be 10 mg/kg for soil and 0.1 mg/L for water samples (Hanby 1998). However, this reference provided no information on how these detection limits were established. The upper end of the working calibration range is 1000 mg TPH/kg and 50 mg TPH/L, for soil and water matrices, respectively. When samples exceeded these ranges, a dilution of the sample extract is necessary before performing the Friedel-Crafts reaction.

Cost

The HM 2000 spectrophotometer and data processor (notebook computer and software) cost about \$8000. Each test kit, i.e., one for soils or the one for water, costs \$1000 and comes with enough reagents to prepare 15 samples (and blanks) for analysis. Additional reagents for these kits, allowing for the analysis of another 15 samples, can be purchased for \$250, and cuvettes cost \$25 each. To bring the cost per analysis with the HM 2000 below \$100, the approximate cost of a laboratory TPH analysis, about 120 analyses would be necessary, which would require an initial investment of about \$10,500 (HM 2000, one Hanby Test Kit, seven reagent supply kits, 20 cuvettes).

EXPERIMENTAL METHODS

Laboratory

Commercial performance evaluation (PE) samples (Table 1) and soil and water matrices, fortified with locally obtained petroleum products, were analyzed during the laboratory trials. All of the certified PE materials were packaged in sealed glass ampoules, the soils as 20-g quantities and the waters as a 1-mL concentrate in methanol (MeOH). After an ampoule containing a PE soil sample was opened, a 5.0 ± 0.2 -g portion was poured directly into a VOA vial containing an extraction solvent. While the soil

was being transferred, the VOA vial was positioned on a balance, so that the desired weight could be measured. The binary solvent mixture was used for preparing samples for the visual and HM 2000 methods of analysis, and MeOH was used with the gasoline-contaminated soils for the CRREL reference analysis method. The PE water sample concentrates were diluted in organic free water (Millipore) to a 1- or 2.5-L volume (Table 1). After dilution, these aqueous samples were handled as described below for the fortified laboratory water samples.

For the laboratory-fortified samples, stock standards were prepared from locally obtained gasoline and diesel fuel by transferring weighed quantities into an appropriate solvent. Gasoline was diluted into MeOH and diesel fuel into methylene chloride. For soil, 5.0 ± 0.1 g of air-dried or moist sample was transferred to a 5-mL glass ampoule using a spatula, weighing dish, funnel, and an analytical balance. Soil samples were spiked by adding small volumes (less than 0.0125 mL) of stock standard to achieve the desired target concentration (Table 2). A syringe (Hamilton) with an extra long needle (7 cm) was used to deliver the spike beneath the surface of the soil. In some cases, an aliquot (0.1 to 0.5 mL) of organic free water was added right after the analyte spike to create a known moisture content. Immediately after these solutions were injected into soils, the

Table 1. Performance evaluation samples used for the laboratory trials. These certified standards were purchased from Environmental Resources Associates, Arvada, Colorado.

Matrix	Name (ID)	Sample wt. or vol. (g or mL)	Certified concentration (perf. acc. limit)*
I. Gasoline			
Soil	Cat. No. 763 Lot. No. 40016	20 g	510 mg TPH/kg (189–712)
Soil	Cat. No. 763 Lot. No. 40020	20 g	1130 mg TPH/kg (403–1600)
II. No. 2 Diesel			
Soil	Cat. No. 765 Lot. No. 40018	20 g	401 mg TPH/kg (194–509)
Soil	Cat. No. 765 Lot. No. 40017	20 g	1730 mg TPH/kg (838–2210)
III. No. 2 Diesel in water			
Water	Cat. No. 764 Lot. No. 50022	1000 mL†	0.903 mg TPH/L (0.297–1.120)
Water	Cat. No. 764 Lot. No. 50022	2500 mL	0.360 mg TPH/L (0.119–0.448)

* Performance acceptance limits.

† Volume of water to which certified stock standard was added.

Table 2. Laboratory prepared matrix spike samples.

Matrix	Standard		Sample		Target concentration
	Conc. (mg TPH/mL)	Vol. (μ L)	Wt. or Vol.	Moisture (%)	
I. Gasoline –Soils					
Silt/Clay	52	10	5.0 g	10	100 mg TPH/kg
Silt/Clay	260	10	5.0 g	10	520 mg TPH/kg
Clay	52	10	5.0 g	10	100 mg TPH/kg
Clay	260	10	5.0 g	10	520 mg TPH/kg
Silt/Clay/Sand	100	10	5.0 g	15	200 mg TPH/kg
Silt/Clay/Sand	520	10	5.0 g	15	1000 mg TPH/kg
Silt	100	10	5.0 g	20	200 mg TPH/kg
Silt	520	10	5.0 g	20	1000 mg TPH/kg
Silt/Clay/Sand	10	10	5.0 g	16	20 mg TPH/kg
II. Diesel–Soils					
Slit/Clay	84	12.5	5.0 g	20	210 mg TPH/kg
Silt/Clay	340	12.5	5.0 g	20	850 mg TPH/kg
Slit	84	12.5	5.0 g	20	210 mg TPH/kg
Silt	340	12.5	5.0 g	20	850 mg TPH/kg
Silt/Clay/Sand	84	12.5	5.0 g	15	210 mg TPH/kg
Silt/Clay/Sand	340	12.5	5.0 g	15	850 mg TPH/kg
III. Gasoline –water					
Water	7.4	50	1050 mL	—	0.35 mg TPH/L
Water	7.4	150	1050 mL	—	1.0 mg TPH/L
Water	7.4	700	1050 mL	—	4.9 mg TPH/L
Water	7.4	2000	1050 mL	—	14 mg TPH/L
Water	6.9	300	1050 mL	—	2.0 mg TPH/L
Water	6.9	3.0	1050 mL	—	20 mg TPH/L

glass ampoules were heat-sealed using a propane torch and then stored in a refrigerator ($4 \pm 2^\circ\text{C}$) for 2 to 7 days to allow the analytes to sorb to the matrix. If held longer than this, the samples were stored in a freezer ($-12 \pm 5^\circ\text{C}$) until they were prepared for analysis. For this preparation, an ampoule was placed into a VOA vial containing an extraction solvent. Once the VOA vial was capped, it was shaken, causing the ampoule to break so that the spiked soil could be dispersed into the extraction solution. Soils prepared for the visual and HM 2000 analysis methods were dispersed over a 30-minute period by intermittent manual shaking before 4.2 mL of the binary solvent was decanted into cuvettes.

For the gasoline-fortified water samples, spikes were added to 1050 mL of organic free water (Millipore) in a 1-L glass bottle with a Teflon-lined septum cap. These samples were made and analyzed on the same day. After fortification, the bottle was inverted several times to mix the contents and then allowed to stand for several minutes. For the reference analysis, a 20-mL glass bottle with a Teflon-lined septum cap was completely filled and immediately capped. For the test method, 500 mL was gently poured into a separatory funnel. Carbon tetrachloride (5 mL) was added to the funnel and the

extraction was performed, as described previously. After a 4.2-mL aliquot of extraction solvent was removed and placed into a cuvette, the funnel was cleaned, and a second set of samples was taken from the 1-L bottle. These replicate samples were taken approximately 20 minutes after the first set. For the reference analysis method, a 2- or 10-mL volume was removed from the VOA vials to a small graduated cylinder and then transferred to an analysis vessel (20-mL VOA vial). When only a 2-mL volume of sample was transferred, 8 mL of organic free water was present in the VOA vial. Care was taken during these transfers to limit exposure while pouring; however, some losses were expected because of these transfer steps.

Field

For the technology demonstration trial, 90 samples (52 field and 38 quality assurance [QA]) samples were distributed for on-site visual and HM 2000 analysis (Table 3). The

field demonstration used a single and double blind format. On site, the technology developer was only informed of the type of TPH contamination, and in the case of soil, the sample weight. At the same time that samples were collected and prepared for distribution for on-site analysis, co-located samples or sample splits were taken for off-site analysis. A description of the field sampling and subsampling methods used during this technology dem-

Table 3. Quality assurance and field samples distributed during the field trials.

	Field		Matrix			Total
	Samples	Duplicate	Bulk*	Spike dup.	PE†	
I. Gasoline (b.p. 60–170°C)						
Soil	9	2	1	2 (4)**	4	20
Water	6	1	1	2 (4)	4	16
II. Diesel/bunker C (b.p. 160–400°C)						
Soil	12	2	1	2 (4)	8	27
Water	12	1	1	2 (4)	—	18
III. Motor oil (b.p. 315–540°C)						
Soil	6	1	—	1 (2)	—	9

* Blank.

† Performance evaluation samples.

** Numbers in parenthesis are the total number of matrix spike samples.

onstration has been presented elsewhere (Hewitt 2000). The field sampling was collaboratively designed to ensure that 1) the number and type of samples could be processed in the time allotted, and, more importantly, 2) that, during the collection and handling of the samples, they would not be compromised. This second objective applies to how representative the samples would be of the in-situ conditions, and to potential sources of determinant error that would compromise the comparison between the different methods of preparation and analysis. In general, the procedures used for this field exercise were similar to the laboratory procedures described previously.

At least one replicate of each sample was sent for reference laboratory analysis. The primary reference laboratory used for this field demonstration, which was the only laboratory to be sent an entire set of replicate samples, failed to produce reliable results (Hewitt 2000). For this reason only QA samples, and those field samples analyzed at CRREL, will be discussed. The QA samples used for field study were composed of PE samples, matrix spike samples, and field sample duplicates (App. A, Tables A1 to A5). Three different types of petroleum contamination—gasoline, diesel/bunker C fuel, and motor oil (i.e., residual)—were examined. Replicates of all the field and QA samples with gasoline contamination were returned to CRREL for analysis using a reference method.

Reference analysis method

For both the laboratory and field trials, replicates of each sample contaminated with gasoline were analyzed at CRREL. The sample preparation and quantification procedure used was consistent with U.S. EPA Method 5021/8021, which is a headspace (HS) sample introduction system coupled to a gas chromatograph (GC) equipped with a photo ionization detector (USEPA 1986). The instrumentation used was a Tekmar 7000 automated HS system, coupled to a SRI model 8610-0058 GC. The instrumental settings were consistent with what has been previously reported (Hewitt 1995).

Soil samples were extracted with MeOH, and a small (less than 0.2 mL) aliquot of this extract was transferred to 10 mL of organic free water saturated with sodium chloride for HS/GC analysis. Water samples were run directly by transferring 0.5 to 10 mL into an analysis VOA vial that contained the appropriate volume of organic free water to bring the final volume to 10 mL. To eliminate variations that exist among different sources of petroleum products and commercial standards,

the same stock standard that was used for spiking the laboratory and field matrix samples was used to prepare the calibration standards. The PE samples (Table 4) were quantified against commercial reference standards.

RESULTS

Laboratory study

Tables 4 through 8 show the results of the HM 2000 laboratory trials. The values reported in these tables, and all of the others covering the field trials, are based on moist weight for the soil samples, and were rounded to two significant figures or less. A single significant figure was reported when the value was limited by the instrumental display of the HM 2000 or by the concentrations provided with the visual comparison chart.

Table 4. Concentration estimates (mg/kg) of total petroleum hydrocarbons (TPH) for performance evaluation soil standards analyzed during the laboratory trials.

Catalog / lot numbers	Certified concentration	CRREL	Visual	HM 2000
a. Gasoline				
763/40016	510	460	200	380
763/40016	510	400	200	330
763/40016	510	430	200	300
763/40016	510	450	200	370
		440±26*	200	340±37
		(86%)†	(39%)	(67%)
		[6%]**		[11%]
763/40020	1130	960	600††	1400††
763/40020	1130	1000	600††	1900††
763/40020	1130	1000	600††	1600††
763/40020	1130	1000	600††	2000††
		990±20	600	1700±270
		(88%)	(53%)	(150%)
		[2%]		[16%]
b. Diesel				
765/40018	401		250	600
765/40018	401		250	630
765/40018	401		250	660
765/40018	401		250	580
			250	620±35
			(62%)	(130%)
				[5.6%]
765/40017	1730		1000‡	2600‡
765/40017	1730		1000‡	2600‡
765/40017	1730		1000‡	4100‡
765/40017	1730		1000‡	4000‡
			1000	3300±840
			(58%)	(190%)
				[25%]

* Average and standard deviation.

† Percent recovery relative to the certified concentration.

** Relative standard deviation.

†† Extract diluted 2.5 mL to 5.0 mL (2x) for visual and MH 2000 analysis.

‡ Extract diluted 1.0 mL to 5.0 mL (5x) for visual and MH 2000 analysis.

Table 5. Concentration estimates (mg/L) of total petroleum hydrocarbons (TPH) for performance evaluation diesel in water standards analyzed during laboratory trials.

Catalog / lot numbers	Certified concentration	Visual	HM 2000
764/50022*	0.903	1.5	3.6
764/50022	0.903	1.5	3.5
764/50022	0.903	1.5	3.6
764/50022	0.903	1.5	3.6
		1.5	3.6±0.05**
		(170%)†	(400%)
			[1.4%]††
764/50022‡	0.360	1.0	2.2
764/50022	0.360	1.0	2.1
764/50022	0.360	0.5	0.6
764/50022	0.360	0.5	0.4
764/50022	0.360	1.0	1.8
764/50022	0.360	1.0	2.1
764/50022	0.360	1.0	2.2
	0.86	1.6±0.78	
	(240%)	(440%)	
		[49%]	

* Concentrated QA standard diluted 1.0 mL to 1.00 L.

† Percent recovery relative to the certified concentration.

** Average and standard deviation.

†† Percent relative standard deviation.

‡ Concentrated QA standard diluted 1.0 mL to 2.50 L.

The results for the PE soil samples (Table 4) show that HM 2000 tended to overestimate the amount of TPH present (three out of four cases), and in only one case was it capable of yielding an average value that fell within the performance acceptance limits (Table 1). The HM 2000 had the same problems with the PE water samples (Table 5). The visual method of analysis and a reference method (for gasoline) consistently yielded TPH concentration estimates that were within the performance acceptance limits for the PE soil samples (Table 1). For the PE water samples, however, the visual method also gave TPH values that were above of the acceptance limits, but they were not as aberrant as the HM 2000 estimates.

The results obtained with the HM 2000 for laboratory soils spiked with gasoline and diesel fuel were often in good agreement with the target concentrations (Tables 6 and 7). In 10 out of 13 cases, the estimates with the HM 2000 were within ±22% of the target concentration, and often were closer to the target value than the visual method. The opposite trend was seen for the laboratory spiked water samples (Table 8), where the HM 2000 estimates ranged from a false negative to an overestimation of the target TPH concentration by factor of three. The visual estimates were within ±50% of the target values. The reference method provided TPH con-

Table 6. Average concentration estimates (mg/kg) and standard deviations of total petroleum hydrocarbons (TPH) for laboratory soil samples spiked with gasoline.

Soil type and target value	CRREL	Visual	HM 2000
Silt			
100 mg TPH/kg*	100±5 (100%)† [5%]**	50 (50%)	78±2 (78%) [2.6%]
520 mg TPH/kg*	550±13 (106%) [2%]	200 (38%)	440±52 (85%) [12%]
Clay			
100 mg TPH/kg*	100±1 (100%) [1%]	50 (50%)	86±9 (86%) [10%]
520 mg TPH/kg*	540±15 (104%) [3%]	200 (38%)	480±74 (92%) [15%]
Silt/Clay/Sand			
200 mg TPH/kg*	190±1 (95%) [1%]	150 (75%)	160±10 (80%) [6%]
1000 mg TPH/kg*	1100±50 (110%) [5%]	>500	>1000
Silt			
200 mg TPH/kg*	200±4 (100%) [2%]	150 (75%)	130±9 (65%) [7%]
1000 mg TPH/kg*	1100±15 (110%) [1%]	>500	>1000
Silt/Clay/Sand			
20 mg TPH/kg††	21±0.5 (105%) [2%]	1–10	19±5.8 (95%) [31%]

* n = 3.

† Percent recovery relative to target value.

** Percent relative standard deviation.

†† n = 7.

centrations for the soil and water matrices contaminated with gasoline (Tables 8 and 10) that were with ±21% and, frequently (12 out of 16), within ±10% of the target value.

The percent relative standard deviations (%RSD) for the HM 2000 measurements were below 25% for all but one of the PE soil and water samples (Tables 4 and 5). The PE sample that showed a %RSD greater than 25% had a concentration near the reported detection limit (Table 5). With two exceptions, the %RSDs for the HM 2000 values were below 35% for the triplicate soil matrix spikes (Tables 6 and 7). The %RSDs established by the reference method for the PE and spiked soil and water samples were 10% or less. Because the visual estimates arise from a discontinuous scale and

Table 7. Average concentration estimates (mg/kg) and standard deviations of total petroleum hydrocarbons (TPH) for laboratory soil samples spiked with diesel fuel.

<i>Soil type and target value</i>	<i>Visual</i>	<i>HM 2000</i>
Silt/Clay/Sand		
210 mg TPH/kg*	150 (72%)†	74±26 (35%) [35%]**
850 mg TPH/kg*	>500	980±14 (110%) [1%]
Slit		
210 mg TPH/kg*	150 (72%)	340±110 (160%) [32%]
850 mg TPH/kg*	>500	930±110 (110%) [12%]
Slit/Clay		
210 mg TPH/kg*	150 (72%)	170±87 (81%) [51%]
850 mg TPH/kg*	>500	920±33 (110%) [4%]

* n = 3.

† Percent recovery relative to target value.

** Percent relative standard deviation.

are subjective, a precision assessment is not meaningful. To estimate precision among sample duplicates, the relative percent differences (RPDs) were used. The RPDs in Table 8 for the HM 2000 TPH estimates indicate that this measurement method may be less precise for water than for soil samples.

For one soil and one water matrix, seven sample replicates were prepared and analyzed to estimate method detection limits (MDLs) for the HM 2000 (Federal Register 1984). The soil matrix was treated with a target concentration of 20 mg TPH/kg and the MDL was calculated to be 17 mg TPH/kg. Seven water PE samples at a certified concentration of 0.36 mg TPH/L were prepared and analyzed, giving an MDL estimate of 2.3 mg TPH/L.

Field study

During a two and one-half day field exercise, 90 samples were distributed for on-site analysis: 36 on the first day, 52 on the second, and 2 on the third. The HM 2000 system experienced instrumental failures on both the first and second days of the field exercise. The second failure could not be corrected in the field, so 38 samples were removed from the site for analysis at a later date. Because of these problems, no TPH values

Table 8. Average concentration estimates (mg/L) and standard deviations of total petroleum hydrocarbons (TPH) for organic free (Millipore) water spiked with gasoline during laboratory trials.

<i>Target value</i>	<i>CRREL</i>	<i>Visual</i>	<i>HM 2000</i>
0.35 mg TPH/L*	0.30±0.01 (86%)† [3%]**	0.25 (71%)	<0.05
1.0 mg TPH/L*	0.90±0.07 (90%) [10%]	1.25 (120%)	0.5±0.6 (50%) [160%]
4.9 mg TPH/L*	4.5±0.17 (92%) [4%]	2.5 (51%)	9.6±0.8 (200%) [8%]
14 mg TPH/L*	11±1.2 (79%) [16%]	10 (71%)	>50
2.0 mg TPH/L*	1.9±0.1 (95%) [11%]	1.5 (75%)	6.9±2.9 (340%) [61%]
20 mg TPH/L*	16±0.8 (80%) [6%]	10 (50%)	>50

* n = 2.

† Percent recovery relative to target value.

** Relative percent difference.

were reported during the technology demonstration, but a preliminary data report was made available 3 days later. Of the 90 samples distributed, 52 (58%) had been analyzed on-site by the visual method, and 47 (53%) by the HM 2000. A final data report was available 12 days after the end of the field exercise.

The TPH results for all of the samples distributed during the field study can be found elsewhere (Hewitt 2000). Appendix A contains the visual and HM 2000 values reported for samples contaminated with gasoline and for all the QA samples (PE, matrix spike samples, and field sample duplicates). Also included in these tables are the values produced by the CRREL reference method of analysis for those samples contaminated with gasoline.

For the PE samples, the recoveries of TPH estimated by the visual method and HM 2000 were all biased high, ranging from 1.6 to greater than 4 times higher than the certified values (Table 9). In particular, the average values reported for the only PE water sample were very high (more than 400% recovery). In contrast, the reference method provided average recoveries that were within ±5% of the accepted or expected values (Table 9). For the matrix spike samples, average values within ±25% of the expected concentration were attained for two out of eight of the duplicate sets by the visual method,

Table 9. Percent recoveries and relative standard deviations for performance evaluation materials analyzed during the field trial.

Sample No./ID	CRREL % Recovery (% RSD)*	Technology developer	
		Visual % Recovery (% RSD)	HM 2000 % Recovery (% RSD)
1. Gasoline			
Soil, SG-1, 2, 3 & 4 (200 mg TPH/kg)	99 (8.6)	160	310 (38)
Water, WG-1, 2, 3 & 4 (1.0 mg TPH/L)	100 (7.0)	430	480 †
2. Diesel			
Soil, SDM-1, 2, 3 & 4 (401 mg TPH/kg)	—	300	270 (56)
Soil, SDM-25, 26, 27 & 28 (2480 mg TPH/kg)	—	270	290 (35)

* % Relative standard deviation

† Only two of the four replicates were analyzed; no estimate was

and for one out of seven by the HM 2000 method (Table 10). However, in one instance, for the visual method, this was clearly fortuitous, as the replicate values differed by a factor of 3.9 (Appendix A, Table A1; SG-20 and -21). The reference method yielded an average TPH concentration within $\pm 20\%$ of the expected value for three of the four duplicate sets analyzed (Table 10).

For the PE samples, the %RSD ranged from 35 to 56% for the HM 2000. In contrast, the %RSDs were below 10% for the reference method of analysis. The RPDs for the matrix spike sample duplicates and field sample duplicates were also used to assess precision. For the matrix spikes, the RPDs ranged up to 140%, and were on average 35%, for the HM 2000 method; in contrast, with the reference method, they ranged up to 28%, and were on average less than 10% (Table 10 and 11).

Of the field samples, 11 co-located soil samples and 8 replicate water samples contaminated with gasoline were analyzed by the HM 2000, visual method, and a reference method (App. A, Tables A1 and A2). Of these 19 sample sets, five had concentrations below detection,

as determined by a reference method, and, for one sample set, only greater than values (those above method calibration range) were reported for both the HM 2000 and visual method. For the 13 remaining sample sets, the reference method and both the HM 2000 and visual results were compared by looking at the percent difference (%D) among them (Fig. 2). For both matrices, at least half the %D values were greater 100%, indicating that both the visual and HM 2000 methods tend to give results that are biased high, compared to the reference method.

DISCUSSION

The procedures developed for using the Hanby Test Kits and HM 2000 to estimate the TPH concentrations in soil and water matrices are easy to learn and use; however, some changes and improvements are recommended. The current practice for collecting and preparing soil samples suspected to be contaminated with gasoline must be changed. The high vapor pressures (i.e., low boiling points) of many of the hydrocarbons in gasoline make the matrices contaminated with this petroleum product, particularly soils, susceptible to volatilization losses when samples are collected and prepared (Hewitt et al. 1995). For this reason, to limit exposure during collection, a modified syringe or similar coring device should be used rather than a spoon or spatula. In addition, instead of adding a soil to a beaker, weighing, and then adding the extraction solvent, as currently instructed, soil samples should be transferred with special precautions being taken to limit exposure, and placed directly into VOA vials containing the appropriate extraction solvent. This approach to handling soils contaminated with gasoline was used in this study, and is consistent with the guidance given in Method 5035 and D 4547-98 (U.S. EPA 1986, ASTM 1998).

To reuse the cuvettes, the Friedel-Crafts alkylation by-products (e.g., AlCl_3) must be removed, and the vessel washed and dried. However, when water is used to rinse these by-products from the cuvettes, a reaction

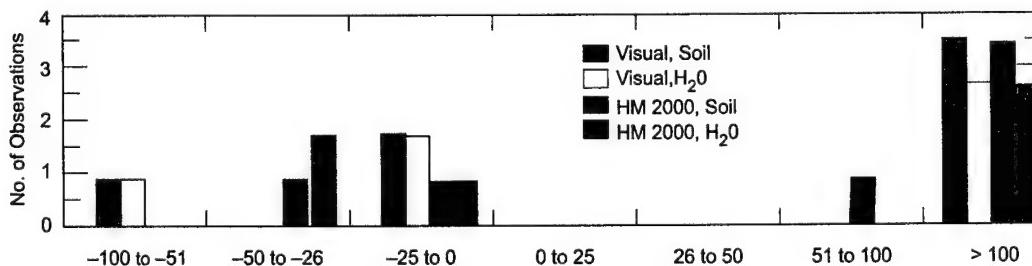


Figure 2. Range of percent difference (%D) values for TPH in soil and water field samples obtained by the visual and HM 2000 methods as compared to the reference method.

Table 10. Percent recoveries and relative percent differences established for the matrix spike duplicates.

Sample No./ID	CRREL % Recovery (% RPD)*	Technology developer	
		Visual % Recovery (% RPD)	HM 2000 % Recovery (% RPD)
1. Gasoline			
Soil, SG-6 & 7 (100 mg TPH/kg)	88 (4.5)	170	160 (0)
Soil, SG-20 & 20 (500 mg TPH/kg)	91 (2.2)	98	120 (34)
Water, WG-6 & 7 (0.48 mg TPH/L)	53 (28)	310	IF†
Water, WG-15 & 16 (24 mg TPH/L)	81 (15)	SL**	SL
2. Diesel			
Soil, SDM-6 & 7 (250 mg TPH/kg)	—	180	310 (10)
Soil, SDM-21 & 22 (1000 mg TPH/kg)	—	250	160 (38)
Water, WDM-1 & 2 (0.98 mg TPH/L)	—	70	< 5
Water, WDM-16 & 17 (24 mg/kg TPH/L)	—	170	OR††
3. Motor oil			
Soil, M1 & M9 (1000 mg TPH/kg)	—	95	60 (12)

* Relative percent difference.

† Instrument failure.

** Sample lost.

†† Over range, no dilution made.

occurs that quickly causes a very nauseating, chlorine-smelling gas to form. Therefore, cuvettes should only be rinsed in an exhaust hood. A cleaning chamber, consisting of a washing station and reaction trap containing charcoal and sodium bisulfate, was fabricated by the technology developer to assist with this operation. However, in its current design, it failed to remove all of the by-products, and additional rinses were necessary once the cuvettes were removed from the cleaning chamber. Furthermore, we observed that these cuvettes needed to be cleaned within a couple of hours of introducing the catalyst, or the bottom window became permanently clouded. A combination of the time constraints and need for an exhaust hood with the present cleaning chamber may limit the reuse of these cuvettes during field operations.

The instrumental problems experienced by the HM 2000 during the field exercise indicate that the present system is not robust, even when operated by the developer. Although not mentioned previously, instrumental problems similar to those experienced in the field also plagued the laboratory trials. Intermittent instrument

Table 11. Relative percent differences (RPD) for the sample duplicates.

Sample No./ID	CRREL (%)	Technology Developer HM 2000 (%)
1. Gasoline		
SG-8 & 18	5.1	46
SG-10 & 19	0	67
WG-11 & 14	0	140
2. Diesel		
SDM-12 & 21	—	31
SDM-15 & 22	—	16
WDM-4 & 18	—	24
3. Motor oil		
M7 & M8	—	0

failures, lack of existing calibration models, and design problems delayed and confounded several of the laboratory trials.

It has been stated that both the HM 2000 and visual method of estimating TPH in environmental matrices are capable of producing concentration estimates within $\pm 10\%$ of the concentration found by accepted methods of analysis, when the specific contaminant of concern is known (Hanby 1998). However, this citation provided no experimental evidence for this claim. This level of accuracy ($\pm 10\%$), which is better than what has been reported elsewhere on the basis of interlaboratory studies (Parr et al. 1994), can be achieved by a single laboratory, as demonstrated by the reference method (14 of 23 cases had values within $\pm 10\%$ for the analysis of certified or spiked samples). In contrast, the HM 2000 only achieved this level of agreement for a certified or target value in 5 out of 34 cases (12%), and the visual method only achieved it in 2 out of 36 cases (5%). In all cases where the HM 2000 or visual method gave an average value within $\pm 10\%$ of the certified or targeted concentration, the samples were spiked soils. Figure 3 shows the %D ranges of the values (33 visual, 31 HM 2000, excluding less than or greater than values) found for both methods of analysis for all of the PE and spiked samples used in both the laboratory and field trials. This figure shows that roughly 60% of the visual values for the spiked soils (12 of 21) and waters (7 of 12), and the HM 2000 values for spiked soils (15 of 25), were within $\pm 50\%$ of the certified or targeted values. However, only 1 out of 6 values (17%) attained by the HM 2000 for spiked water samples fell within this range. Clearly, neither method is capable of routinely achieving a $\pm 10\%$ accuracy. With the exception of HM 2000 analysis of water matrices, perhaps they can achieve a $\pm 50\%$ level of accuracy, in the majority of cases. It should be noted that, in comparison to the reference method for the analysis of field samples, this

level of agreement was not obtained, that is, less than a majority of values were within $\pm 50\%$ (Fig. 2).

The Hanby Test Kits and the visual method of analysis are currently recognized by the U.S. Environmental Protection Agency as a reliable field screening method for TPH in environmental matrices. The highest data-quality level that has been assigned to these techniques states that they are capable of producing TPH values that are within an order of magnitude of the true or accepted concentration (USEPA 1997). The performance of the visual method of analysis for the PE and matrix spike samples analyzed during both the laboratory and field trials supports this classification, as there were no TPH values outside of this range. Indeed, there were only a couple of values for the visual method of analysis that were a factor of 5 \times or slightly greater than the expected concentration. In comparison to the visual method of analysis, the HM 2000 yielded some values that were false negatives and one that was greater than the expected value by more than 10 \times .

The detection limit for water samples for both the visual and HM 2000 methods is claimed to be 0.1 mg TPH/L (Hanby 1998). However, the MDL estimated during the laboratory trials was 2.3 mg TPH/L. Furthermore, all of the values given by the HM 2000 that either were false negatives or that were more than 10 \times greater than the expected concentration were for water samples spiked at a concentration below 1.0 TPH mg/L. The MDL estimated during the laboratory trials for a soil matrix (17 mg TPH/kg) was in reasonable agreement with the reported value (10 mg TPH/kg, Hanby 1998). Since there was agreement for the detection limit with respect to soils, and no false negatives or estimates greater than 10 \times the expected concentration were observed for spiked soils, the HM 2000 system appears to be better suited for this matrix.

SUMMARY

This study was undertaken to substantiate claims that a spectrophotometric analysis of the colored catalyst

resulting from a Friedel-Crafts reaction could characterize the type and amount of petroleum contamination in environmental matrices. With respect to a qualitative interpretation, the HM 2000 spectrophotometer is currently only capable of providing a spectral display that must be interpreted subjectively and, therefore, it is no further advanced than the visual method of analysis. For a quantitative estimate of a petroleum product, whether it is an individual compound or a mixture, as in a fuel, an appropriate calibration model must be available and selected before samples are prepared and analyzed. When these requirements were met, results from laboratory and field trials for both the visual and HM 2000 method of analysis were often similar for assessing TPH contamination. When a data-quality level that specifies that the TPH estimates must be within an order of magnitude of the certified or expected value was applied, the HM 2000 yielded some values for water samples that failed this criterion. This level of data quality was appropriate for the visual method of analyzing both soil and water matrices, and, for the HM 2000, with respect to soil samples. Aside from this, other claims regarding the accuracy or detection limit of both the visual and HM 2000 methods could not be substantiated. The most troublesome finding of this evaluation, however, is that, currently, the HM 2000 system is prone to software related failures that interrupt routine operation. On the basis of these observations, findings, and the associated costs, the current HM 2000 system is not recommended for the characterization of petroleum products in environmental matrices.

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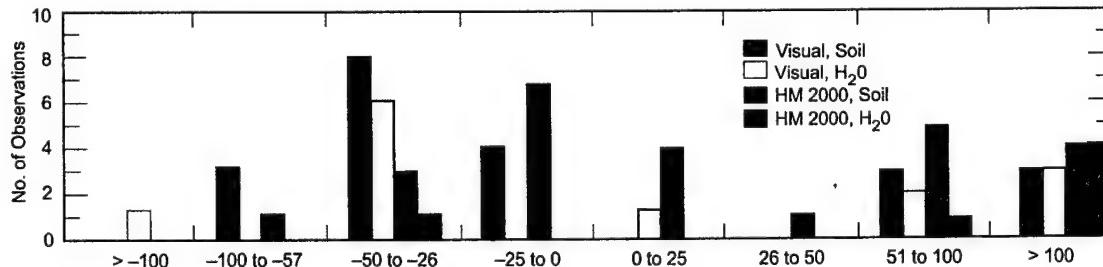


Figure 2. Range of percent difference (%D) values for TPH in soil and water quality assurance samples obtained by the visual and HM 2000 methods.

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APPENDIX A: SELECTED RESULTS FROM THE TECHNOLOGY DEMONSTRATION TRIAL

Table A1. Concentrations (mg/kg) of total petroleum hydrocarbons (TPH) in soil samples contaminated with gasoline.

Sample no./ID	CRREL	Technology developer	
		Visual	HM 2000
SG-1/PE (200)*	200	200	740
SG-2/PE (200)	180	500	750
SG-3/PE (200)	220	400	740
SG-4/PE (200)	190	170	270
SG-6/Matrix-Spike (100)	86	200	160
SG-7/Matrix-Spike (100)	90	140	160
SG-20/Matrix-Spike (500)	450	250	720
SG-21/Matrix-Spike (500)	460	730	510
SG-5/Matrix-Blank	<1	10	2.2
SG-8/Sample	19	50	72
SG-18/Sample Duplicate (SG-8)	20	80	79
SG-10/Sample	<1	20	14
SG-19/ Sample Duplicate (SG-10)	<1	10	11
SG-9/Sample	4400	8300	11000
SG-11/Sample	5800	5100	9200
SG-12/Sample	13000	12000	12000
SG-13/Sample	14	49	30
SG-14/Sample	<1	21	21
SG-15/Sample	980	360	720
SG-16/Sample	<1	5	18

* Values in parenthesis are the spiked concentration mg TPH/kg or the sample duplicate.

Table A2. Concentrations (mg/L) of total petroleum hydrocarbons (TPH) in water samples contaminated with gasoline.

Sample no./ID	CRREL	Technology developer	
		Visual	HM 2000
WG-1/PE (1.0)*	0.93	4.3	4.8
WG-2/PE (1.0)	0.99	5.0	4.8
WG-3/PE (1.0)	1.0	1.0	IF†
WG-4/PE (1.0)	1.1	7.0	IF
WG-6/Matrix Spike (0.48)	0.29	0.5	IF
WG-7/Matrix Spike (0.48)	0.22	2.5	5.2
WG-15/Matrix Spike (24)	18	SL**	SL
WG-16/Matrix Spike (24)	21	SL	SL
WG-11/Sample	1.2	1.0	1.0
WG-14/Sample Duplicate (WG-11)	1.2	4.0	5.3
WG-5/Matrix Blank	<0.05	<0.1	<0.05
WG-8/Sample	37	30	22
WG-9/Sample	11	5.0	7.0
WG-10/Sample	7.7	>30	>50
WG-12/Sample	3.6	10	11
WG-13/Sample	0.95	2.0	2.0

* Values in parenthesis are the spiked concentration mg TPH/kg or the sample duplicate.

† Instrument failure.

** Sample lost during preparation.

Table A3. Concentrations (mg/kg) of total petroleum hydrocarbons (TPH) in soil samples contaminated with diesel and bunker C fuel.

Sample no./ID	Technology developer	
	Visual	HM 2000
SDM-1/PE (401)*	810	900
SDM-2/PE (401)	1500	950
SDM-3/PE (401)	2000	580
SDM-4/PE (401)	690	2000
SDM-25/PE (2480)	6800	7700
SDM-26/PE (2480)	9000	8500
SDM-27/PE (2480)	4900	3500
SDM-28/PE (2480)	6000	9000
SDM-6/Matrix Spike (250)	480	740
SDM-7/Matrix Spike (250)	400	820
SDM-23/Matrix Spike (1000)	2500	1300
SDM-24/Matrix Spike (1000)	2500	1900
SDM-12/Sample	7500	19000
SDM-21/Sample Dup. (SDM-12)	7500	26000
SDM-15/Sample	15000	17000
SDM-22/Sample Dup. (SDM-15)	18000	20000
SDM-5/Matrix Blank	48	20

* Values in parenthesis are the spiked concentration mg TPH/kg or the sample duplicate.

Table A4. Concentrations (mg/L) of total petroleum hydrocarbons (TPH) in water samples contaminated with diesel and bunker C fuel.

Sample no./ID	Technology developer	
	Visual	HM 2000
WDM-1/Matrix Spike (0.98)*	0.84	<0.05
WDM-2/Matrix Spike (0.98)	0.5	<0.05
WDM-16/Matrix Spike (24)	30	8.6
WDM-17/Matrix Spike (24)	50	>50
WDM-4/Sample	13	33
WDM-18/Sample Dup. (WDM-4)	17	26
WDM-15/Matrix Blank	<1	<0.05

* Values in parenthesis are the spiked concentration mg TPH/kg or the sample duplicate.

Table A5. Concentrations (mg/kg) of total petroleum hydrocarbons (TPH) in soil samples contaminated with motor oil.

Sample no./ID	Technology developer	
	Visual	HM 2000
M1/Matrix Spike (1000)*	1000	630
M9/Matrix Spike (1000)	900	560
M7/Sample	12000	22000
M8/Sample duplicate (M7)	24000	22000

* Values in parenthesis are the spiked concentration mg TPH/kg or the sample duplicate.

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<p>The H.E.L.P. Mate 2000 (HM 2000) is a spectrophotometric instrument developed for use with the Hanby Test Kits to rapidly assess of total petroleum hydrocarbon contamination (TPH) in environmental matrices on site. This spectrophotometer is designed to remove the subjectivity associated with the present visual method of analysis, and to eliminate the requirement for prior knowledge of the type of petroleum hydrocarbon contamination present at a given site. Both the HM 2000 and the current visual method of analysis measure the color that is produced by the Friedel-Crafts reaction with the aromatic hydrocarbons present in petroleum-based fuels, oils, and solvents. Laboratory and field studies were used to evaluate the HM 2000. Different results were obtained, depending on the type of sample matrix. In general, the HM 2000 was more accurate and precise for soil samples than for water samples. However, in comparison to the visual method, the HM 2000 was neither as accurate nor did it offer any qualitative advantages.</p>					
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